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1 **Design and operation of an inexpensive, laboratory-scale,**  
2 **continuous hydrothermal liquefaction reactor for the**  
3 **conversion of microalgae produced during wastewater**  
4 **treatment**

5  
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17 **Abstract**

18 Recently, much research has been published on the hydrothermal liquefaction (HTL) of  
19 microalgae to form bio-crude, which can be further upgraded into sustainable 3<sup>rd</sup> generation  
20 biofuels. However, most of these studies have been conducted in batch reactors, which are not  
21 fully applicable to large-scale industrial production. In this investigation an inexpensive laboratory  
22 scale continuous flow system was designed and tested for the liquefaction of microalgae  
23 produced during wastewater treatment. The system was operated at a range of temperatures

(300 °C – 340 °C) and flow rates (3 – 7 ml min<sup>-1</sup>), with the feed being delivered using high pressure N<sub>2</sub> rather than a mechanical pump. The design incorporated the *in-situ* collection of solids through a double tube design. The algae was processed at 5 wt% and the results were compared to those from a batch reactor operated at equivalent conditions. By combining high heating rates with extended reaction times, the continuous system was able to yield significantly enhanced bio-crude yields compared to the batch system. This demonstrates the need for inexpensive continuous processing in the lab, to aid in scale up decision making.

## 1 Introduction

Hydrothermal liquefaction (HTL) of microalgae represents a promising pathway for the production of sustainable, 3<sup>rd</sup> generation biofuels [1]. It converts the entire algae, including proteins and carbohydrates as well as lipids, and can therefore use faster growing, and cheaper algae than conventional lipid-based processes [2]. It is conducted at high water loadings, typically ranging from around 80 wt% to 95 wt% [3], significantly reducing the algae drying requirements, and saving up to 90 % of the total energy costs associated with algal harvesting [4]. Finally, HTL allows a significant proportion of the nitrogen and phosphorus initially present in the algae to partition into the water phase, facilitating the recovery and recycling of these valuable resources [5-7].

At the same time, HTL reactions require high pressures to maintain water in its liquid phase, and prevent the latent heat losses associated with vaporisation [1]. Based on steam tables, minimum reaction pressures can be calculated to range from 64 bar to 210 bar for typical reaction temperatures of 280 °C to 370 °C [8]. Furthermore, the reaction involves a thick biomass slurry, containing algal particles suspended in an aqueous phase and yields four different product phases (solids, biocrude oil, water and gas), which all need to be collected and separated post reaction. This makes it difficult to carry out this process under continuous flow in a laboratory environment. Consequently, the vast majority of algal HTL research has been conducted within

batch reactors. Although batch systems allow the evaluation and comparison of different feedstocks and reaction conditions, they are not directly applicable to large-scale industrial processing, which heavily relies on continuous flow processes with much higher volumetric productivities [9]. Furthermore, batch systems are unable to provide the same level of control as continuous flow systems and struggle to combine high heating rates, which have been shown to be beneficial for higher biocrude yields [10, 11], with extended reaction times, required to achieve full biomass conversion.

Only few continuous liquefaction studies have been published to date [12-14], and have often been restricted to low algae loadings due to operational problems with the feed delivery pump [15], or the formation of blockages within the product collection system [16]. An exception is the work by Elliott *et al.*, who managed to process a biomass slurry with an algae loading of 35 wt% [17]. Their design employed a modified dual syringe pump system to push the algae through the system, and pre-heated the algae feed inside a continuous stirred tank reactor (CSTR), before introducing it into a plug flow reactor (PFR) for further conversion. However, this design is expensive, and may therefore restrict its widespread use by the wider research community.

Almost all continuous liquefaction experiments described in the literature were conducted in PFRs, with the exception of the work by López Barreiro *et al.*, who employed a CSTR with a reaction temperature of 350 °C and a residence time of 15 minutes [18]. However, using this system, overall bio-crude yields were slightly reduced compared to batch reactions, and this was attributed to the cross-reaction between primary intermediates and final reaction products. In contrast, the results from the PFR systems were generally not compared to equivalent batch data, although both Biller *et al.* [14] and Jazrawi *et al.* [16] reported increased bio-crude yields as the system flowrates were increased.

Another challenge with the HTL process is the tight process economics of producing a relatively low value fuel product. Algae cultivation is relatively expensive and nutrient-intensive [19], and

consequently cost predictions for the production of algal bio-crude via HTL were found to significantly exceed current transportation fuel market prices [20]. It is therefore unlikely that the fuel product will be able to pay for the entire liquefaction process on its own and additional value streams need to be identified and developed which can help to subsidise the fuel production costs. Potential options include the production of by-products with sufficient market share, such as animal feeds, protein supplements, fertilizers or bio-plastics [1], or combining algae cultivation with secondary functions such as carbon sequestration [21-23] or bioremediation [24]. Particularly the combination of algae biomass production with wastewater treatment has the potential to result in substantial cost savings, as well as significantly reducing the overall environmental impact of the two processes [25]. One of the main objectives of wastewater treatment is the removal of nutrients, particularly phosphorus and nitrogen, which can cause eutrophication. Combining wastewater treatment with algae cultivation significantly reduces the amount of additional nutrients required for algae growth [26]. Global municipal waste water production amounts to approximately 300 billion m<sup>3</sup>, of which just over 50 % is currently treated [27]. Consequently there is huge potential, particularly in less-developed economies, to apply algae cultivation to improve water quality whilst producing a sustainable fuel by-product.

In this investigation the design of a continuous lab-based HTL system is presented, specifically designed to represent an inexpensive alternative to laboratory systems already described in the literature. The system was commissioned and operated using a 5 wt% microalgal slurry produced during the bioremediation of domestic wastewater. During the study the effect of the operating temperature and system flow rate were investigated and compared to the results obtained from a transient batch reactor, operated under equivalent conditions (reaction temperature and heating rates).

## 2 Material and methods

### 2.1 Biomass preparation and analysis

The algae used for this project was obtained from a collaboration with the Algae Research Group (Department of Biology and Biochemistry, University of Bath) and a local water company, who cultivated the algae to provide tertiary removal of nitrogen and phosphorus from domestic wastewater. As such, the algae (community of locally sourced *Scenedesmus* and *Chlorella* strains) was specifically selected for its efficiency in phosphate uptake, as well as its ability to settle out quickly to facilitate its recovery following wastewater treatment.

After harvesting, the algae were allowed to settle for a number of days, and the excess water was decanted. The aqueous biomass was subsequently centrifuged to obtain an algal slurry with a biomass concentration of 21.7 wt%, which was separated into 50 g batches and stored at around -4 °C.

For each experiment, the required amount of algae was defrosted and diluted with D.I. water to obtain the desired experimental concentration of 5 wt%. The exact algae loading was determined by oven-drying aliquots of the well-mixed algae slurry.

The algae ash content was determined using thermogravimetric (TGA) analysis of the dried algae, according to literature precedent [28]. The analysis was conducted in air on a Setaram TG-92 microbalance, using a ramp rate of 10 °C min<sup>-1</sup> to 500 °C, followed by a ramp of 20 °C min<sup>-1</sup> to 900 °C. This analysis was repeated with the same ramp rate on a TG-DSC-EGA analyser (Setaram Setsys Evolution TGA 16/18, Pfeiffer Vacuum Omnistar GSD 320), to determine the gas phase composition. The energy density of the dried algae was measured on an IKA® Calorimeter C1 analyser, using a 0.5 g sample, and the weight of the combustion residue was recorded, for comparison.

The carbohydrate assay was carried out according to Taylor [29], incorporating an upfront two-step hydrolysis protocol adapted from Kostas *et al.* [30]. The lipid content was determined post conversion to fatty acid methyl esters (FAMES) using GC-MS analysis, as described previously [31]. The protein content was estimated using the algal nitrogen content and applying the standard Jones' factor of 6.25 [32].

## 2.2 Batch reactions

Batch liquefaction reactions were conducted using the same set-up described in our earlier work [24, 31]. Briefly, it consisted of a 50 mL reactor, fitted with an internal thermocouple and connected to a pressure gauge and vent valve and heated inside a tubular furnace. Each reaction was conducted using approximately 20 g of the pre-mixed algae slurry (5 wt% algae loading). During reactions, the reactor was placed inside the preheated furnace until the desired reaction temperature (300 °C – 340 °C) was reached. At this point, the reactor was immediately removed from the furnace and left to cool in ambient air. Different heating rates (at a constant reaction temperature of 320 °C) ranging from 10.1 °C min<sup>-1</sup> to 52.6 °C min<sup>-1</sup> were obtained by varying the furnace temperature between 500 °C and 800 °C.

Following reactions, the reactor was vented and the reactor contents were decanted through pre-weighted filter paper, to recover the water phase (filtrate). The aqueous residue, defined as the non-volatile material present in the aqueous phase, was determined gravimetrically after removal of the water by overnight drying of the aqueous phase aliquots in a drying oven (> 60°C). The biocrude phase was recovered by rinsing the reactor wall and filter residue with chloroform until the solvent remained clear and evaporating the solvent under vacuum. Solid yields were determined from the mass of retentate collected on the filter paper.

All reactions were conducted in triplicate, and the experimental variation was determined in terms of standard deviations.

## 2.3 Continuous reactor design and operation

### 2.3.1 System design

The continuous-flow liquefaction system used for this study can be divided into a number of sub-sections: a feed delivery system, the liquefaction reactor itself and a product collection and flow control system (Figure 1). The full P&ID is available in the supporting information.

The feed delivery system consisted of two parallel feed reservoirs, pressurised from a high-pressure nitrogen cylinder and connected via a valve manifold. This design allowed each feed reservoir to be isolated in turn, whilst maintaining flow through the other, to enable topping up with algae, or switch-over from water to algae flow and vice versa, without loss of system flow. The system pressure was controlled to between 160 bar and 165 bar using the pressure regulator on the nitrogen cylinder, limiting the maximum reaction temperature to 347 °C.

The reactor consisted of a vertical, double tube design, heated inside a tubular furnace. Cold algae feed entered through the inner tube from the top, where it started to be heated, the products then flowed back up the annulus of the reactor and exited the reactor from the top. This design was chosen to allow fast heating of the algae and collection of the solid products at the bottom of the reactor, preventing their accumulation within the flow line, which would lead to reactor blockages. These solids could then be removed at the end of the reaction. The reaction temperature was determined using a thermocouple (T1) located at the outlet of the inner tube, and a second thermocouple (T2) at the reactor outlet was used to estimate the temperature gradient throughout the reactor.

Batch-wise collection of the liquid reaction products at pressure and elevated temperatures was conducted within two parallel, nitrogen-filled collection pots, similar to the configuration previously employed by Elliott *et al.* [17]. The system flow was controlled indirectly by regulating the flow of nitrogen and reaction gases from the liquid collection pots to a vent line, using a manual gas flow



meter. To protect the flowmeter against overpressure, a pressure-reducing regulator was installed upstream to reduce the pressure below 10 bar. Once one of the pots was full, flow was redirected to the other, and the pot was vented and drained to recover the liquid reaction products. Subsequently, the pot was re-pressured with nitrogen from a separate gas cylinder, and equalized to the system inlet pressure. Following each liquid recovery step, the collected liquid volume and collection time were recorded to monitor and calibrate the system flow rate.

### 2.3.2 System operation

Prior to each reaction run, the system was started up on distilled water and the gas flow from the outlet was adjusted to achieve liquid flow rates ranging from 3 mL min<sup>-1</sup> to 7 mL min<sup>-1</sup>. Next, the furnace temperature was increased gradually until the desired reaction temperature (300 – 340 °C) was obtained, as measured by T1, the thermocouple located at the bottom of the inner reaction tube. Once steady state was reached, the reaction was started by switching system flow from distilled water to the pre-mixed algae slurry. After flowing a total of 1 L of a 5 wt% algae slurry, the system was maintained at reaction conditions, whilst being purged with distilled water for another two hours, until the liquid at the system outlet started to run clear. At this point, the furnace was turned off and water flow was maintained until the system temperature reduced to a safe level, at which point it was isolated and allowed to cool overnight. Depending on the system flow rate, the liquid collection pots were drained every 15 to 30 minutes, to prevent overflow of the reaction liquids into the gas lines. The total collected liquid volume was recorded to determine the remaining feed volume, and prevent the system from running dry.

A repeat run at the medium reaction temperature of 320 °C and flowrate of 5 mL min<sup>-1</sup> was used to estimate the experimental variation of the system.

### 2.3.3 *Product recovery*

Neither the gas yield nor the composition was investigated as the study focused on liquid phase and solid products. Bio-crude and water products recovered from the liquid collection pots were collected and separated using vacuum filtration through pre-weighed filter paper. After each collection interval, a 20 mL aliquot of reaction water was re-filtered by gravity, to ensure full removal of any entrained solids, and retained for further analysis. Any remaining water was re-filtered under vacuum and combined into two separate samples: water collected during algae flow and water collected post reaction, during water purging. The bio-crude product was recovered by washing all filter papers with chloroform and combined into a single fraction. Solid carry-over to the outlet was determined by re-weighing the dried filter papers following bio-crude removal.

At the end of each reaction run, the system was fully dismantled to allow the recovery of solids and bio-crude product residue from the reactor and the system pipework. The reactor contents were filtered and thoroughly washed with water and chloroform to obtain the solid products and a heavy bio-crude fraction, labelled 'heavy bio-crude'. Chloroform washing of the reactor outlet piping and collection pots allowed the recovery of 'pipe bio-crude ', which was eventually combined with the bio-crude product from the system outlet to form the 'light bio-crude' fraction.

Product yields were calculated on a dry biomass basis, without further correction for the ash content.

### 2.4 *Product analysis*

Elemental (CHN) analysis of the bio-crude samples was carried out externally on a Carlo Erba Flash 2000 Elemental Analyser. For the continuous reactions, the light and heavy bio-crude fractions were analysed separately, before calculating weighted averages to determine the elemental distribution to the total biocrude phase. In the case of the batch reactions, only the most

representative of the three repeats (yield closest to average) was analysed for each reaction condition.

The water content of the combined bio-crude from all continuous HTL reactions was determined by Karl Fischer titration. Prior to analysis, the sample was diluted in chloroform to 2 wt%, and calibrated against the chloroform water content. The energy density of the combined bio-crude was measured on an IKA® Calorimeter C1 analyser, using a 0.5 g sample. This analysis was also used to estimate the ash content of the bio-crude and verified against the results from TGA.

The concentration of ammonium ions in the water phase was determined using a Randox Urea analysis test kit. Prior to analysis, the samples were diluted with D.I. water to a concentration of 20 vol%. Subsequently 10 µL of sample was reacted for 5 min with 1000 µL of a urease reactant, followed by the addition of 200 µL of sodium hypochlorite solution to induce the colour change. Finally, the sample absorbance was measured at 600 nm and calibrated using a reagent blank and standard solution.

Total organic carbon (TOC), total inorganic carbon (IC) and total nitrogen (TN) of the water phase products were determined on a Shimadzu Corp. total organic carbon analyser (TOC-L), linked to a total nitrogen analyser (TNM-L) and autosampler (ASI-L). Prior to analysis, samples were diluted with D.I. water to 12.5 vol%. For the continuous reactions, the total carbon and nitrogen recovery to the water phase was estimated using the carbon and nitrogen concentrations in the combined water phase obtained during the entire reaction period.

### **3 Results and discussion**

#### **3.1 Biomass characterization**

Thermogravimetric analysis (TGA) of the dried algae resulted in a total weight loss of 79.2 wt%, associated with the loss of residual moisture (5.0 wt%), two exothermic peaks at temperatures of

350 °C and 545 °C (65.1 wt%) and an endothermic peak at 831 °C (9.1 wt%, supporting information). The two exothermic peaks can be associated with the combustion of organic biomass components, confirmed by the detection of both carbon dioxide and water during TG-MS analysis, whereas the only gas released over the high-temperature endothermic peak was carbon dioxide. Therefore it is likely that this peak was associated with the thermal decomposition of carbonates, as previously detected during TGA analysis of macroalgae [33], and suggests that the wastewater derived algae sequestered atmospheric carbon in both organic and inorganic form. As the ash content is generally defined as the inorganic biomass fraction, it was calculated to include these carbonates by using the residual sample weight at 650 °C. The resulting value of 29.9 wt% compares to a residue weight of only 20.8 wt% at 900 °C and a combustion residue of 30.1 % using bomb calorimetry.

Biochemical compositional analysis of the algae showed that it was predominantly composed of proteins, and contained only low amounts of lipids and carbohydrates (Table 1). Overall, the contribution of these three major biochemical compounds was 59.1wt%, with an ash content of 29.9 wt%., resulting in an energy density of 12.72 MJ kg<sup>-1</sup>.

## 3.2 System design

The system was specifically designed to provide a lower-cost alternative to the HTL systems already used in the literature. During the commissioning process, a number of operational challenges were encountered, which required significant modifications to the initial design, to allow the processing of the entire biomass inventory. Particular challenges were the formation of blockages within the reactor tube itself, and large fluctuations in system flow and temperature, as a result of control valve blockages. In this section, the final design is discussed and compared to alternative systems in the literature.

### 3.2.1 Flow delivery

To date, most continuous HTL systems described in the literature have employed high-pressure mechanical pumps to push the algae feed through the system. However, even though mechanical pumps are the expected method of choice for larger-scale operation, laboratory-scale pumps, that can generate the high required reaction pressure as well as being able to handle the semi-solid algal particles in the feed, (such as the modified dual syringe pump system used by Elliott *et al.* [17]) are expensive, and still not directly applicable to industrial processing. Alternative pumps used in the literature have either exceeded the desired laboratory-scale flow rates, such as the triplex piston pump system used by Jazrawi *et al.* [16] and Cole *et al.* [12] (15-90 L h<sup>-1</sup>) or have struggled to process elevated biomass concentrations, such as the HPLC pump used by Patel and Hellgardt [15].

In contrast, by using high-pressure nitrogen as the algae driving force, our design eliminates the requirement of a mechanical pump completely, and thereby reduces the risk of blockages within the pump cavities as well as representing a lower-cost lab scale alternative to existing HTL systems. It provides a high degree of flexibility, both in terms of flow rate and feed pressure, and the double feed cylinder arrangement allows continuous feeding of algae. Despite initial concerns of nitrogen break-through, resulting in flow fluctuations, the final design was found to be able to deliver a constant liquid flowrate throughout the entire reaction period, as determined from the liquid accumulation within the liquid collection pots, as well as constant reaction temperatures (supplementary information).

A disadvantage is the lack of the precise metering functionality of some of the mechanical pumps, and consequently the system flow rate had to be controlled separately. Furthermore, as nitrogen is a compressible fluid, variations in the pressure drop through the system could have a larger effect on the algae flow rate through the system. This problem was mitigated by controlling the product flow from the outlet instead.

### 3.2.2 Reactor configuration

Consistent with the majority of continuous HTL systems described in the literature, our design employed a modified PFR to conduct the liquefaction reaction. However, to the best of our knowledge this is the first time a double-tube design to allow the collection of the solid reaction products within the reactor itself has been applied to this reaction. The main reason for adapting this arrangement was to address operational problems caused by the extensive formation of blockages within a single-pass, up-flow reactor. These blockages were predominantly attributed to the accumulation of solid products within the reactor tube, possibly as a result of insufficient flow velocities through the system to allow full fluidisation of this phase.

No previous publication reported significant issues with blockages formed within the reactor, however it should be noted that in many cases the algae loadings were significantly lower than in the present work [13, 15, 34], or the authors employed a co-solvent to prevent plugging issues in the first place [12, 15]. An exception is the work by Elliott *et al.*, who processed a feed with an algae concentration of up to 35 wt%, however this group employed a CSTR to pre-heat the algae feed from 133 °C to the final reaction temperature before allowing the reaction to be completed in a PFR [17]. It should also be noted that the algal biomass used in most previous HTL reactions was less challenging to process than the wastewater algae used in this project, which contained a very high ash content (~ 30 %), allowing the algae to settle out quickly following wastewater treatment. This high ash content may have contributed to the severity of the reactor blockages experienced with our initial design.

An additional benefit of the double-tube reactor is that it combines very fast heating rates with extended reaction times, and reduces the presence of hot-spots at the reactor wall, which might catalyse the formation of radicals, which in turn could initiate polymerisation reactions. Based on the range of system flow rates (3 mL min<sup>-1</sup> to 7 mL min<sup>-1</sup>), heating rates were estimated to have ranged from 28.8 °C min<sup>-1</sup> to 67.6 °C min<sup>-1</sup>, whilst the residence time of the hot reagents/products

in the outer tube varied between 17.7 and 41.8 minutes. The design also allowed the partial heat recovery from the hot reaction product in the reactor, without causing the plugging problems reported by Elliott *et al.* when pre-heating a lignocellulosic reaction feed above 133 °C [17]. At the same time, temperature drops between 45 °C and 58 °C were recorded between the bottom of the inner tube and the outlet of the reactor.

The solid retention within the reactor exceeded 95 % for all reactions, with little correlation to the selected reaction conditions (temperature and flow). This suggests that gravity settling was highly effective in the recovery of this solid fraction. Even so, the solid capacity of the reactor is limited, and therefore in future designs it may be necessary to incorporate a solid removal system to allow extended system operation.

### 3.2.3 *Product collection and flow control*

Prior to designing the liquid collection system, consisting of two parallel, nitrogen-filled collection pots, an attempt was made to control the system flow directly, using a liquid flowmeter at the system outlet. However, the high viscosity of the biocrude at room temperature resulted in the clogging of the control valves, causing significant fluctuations of the system flow. Similar problems were previously reported by Jazrawi *et al.*, who experienced significant pressure fluctuations as a result of transient blockages of their back-pressure control valve [16]. In contrast, controlling the system backpressure on the outflow of gas avoided the requirement of having to pass the viscous biocrude through the restrictions within a control valve. Although this design required the batch-wise removal of liquid products, followed by repressurisation of the collection pots, further modifications to install a level controller within the collection pot would allow the continuous recovery of the liquid products. Furthermore, flow control could be improved by installing a liquid flowmeter to set the operating variable of an automatic control valve at the gas outlet.

#### 3.2.4 System operation

During the operation of the system, depending on the reaction temperature and the system flow rate of any particular experiment, the collection pot temperature varied from 56.3 °C to 125.9 °C, as a result of different residence times, and therefore different heat losses to the environment. The percentage of the total recovered bio-crude fraction collected from the outlet was found to be directly proportional to this temperature, whereas the opposite trend was observed for the bio-crude obtained from the reactor outlet piping, post reaction (supplementary information). These trends could be related to increases in the biocrude viscosity and reduced miscibility with the water phase, as the collection temperature is reduced. However, all reactions were conducted with the same amount of algae, and consequently, it is not known whether bio-crude accumulation within the system pipework remained constant over the entire reaction period, or whether it reached a saturation point, after which all additional bio-crude exited from the system. Continuous bio-crude accumulation would eventually result in the formation of system blockages, and therefore system operation should be investigated over longer reaction periods. As the partitioning between bio-crude remaining in the system pipework and bio-crude recovered from the outlet appeared to depend mostly on the collection temperature, these two fractions were combined into a single 'light-biocrude' phase.

In contrast, the fraction of bio-crude recovered from the reactor was found to be independent of the collection temperatures. As this bio-crude cannot be easily recovered from the system during continuous flow and was found to be much more viscous than the biocrude fractions recovered from the outlet and the reactor pipework, which suggests a different chemical composition, it was kept as a separate, 'heavy bio-crude' phase, further GC-MS analysis confirmed the different chemical nature of both bio-crude samples (see supporting information).

Using our system, it was possible to consistently process 1 L of a 5 wt% algae slurry, whilst maintaining constant reaction temperatures and system flow rates. Whilst the system required a



lot of operator input, it represents a significantly lower cost alternative to the systems already used in the literature, making it feasible as a bench-scale laboratory system.

### 3.3 Batch conversion

Prior to converting the wastewater-derived algae within the continuous HTL system, a number of baseline reactions were conducted in a batch system to determine the effect of reaction temperature and heating rate on the resulting product distribution. Batch reactions were conducted under transient conditions, which means that the reactors were removed from the furnace as soon as the desired reaction temperature was reached, giving an effective reaction time of 0 minutes. This approach allows much faster heating rates than the more commonly used isothermal systems, where the reaction temperature is maintained for a prolonged period of time.

#### 3.3.1 *Effect of reaction temperature*

The conversion of the wastewater-derived algae was studied at three different temperatures (303 °C, 322 °C and 339 °C) with a constant furnace temperature of 700 °C, resulting in averaged heating rates ranging from 33.8 °C min<sup>-1</sup> at 339 °C to 37.6 °C min<sup>-1</sup> at 303 °C. As the reaction temperature was increased from 303 °C to 339 °C, solid yields were found to reduce from 43.6 wt% to 38.2 wt% (Figure 2a). This is consistent with our earlier work [31] and can be associated with an increase in algae conversion resulting in reduced solid retention of the organic biomass components. As the reaction temperature was increased from 303 °C to 321 °C, the water phase residue yield also experienced a remarkable decrease from 29.9 wt% to 20.7 wt%, which could be partially attributed to the simultaneous increase in biocrude yield (12.1 wt% to 17.1 wt%) and a reduction in the overall mass balance closure from 85.5 % to 79.2 %. The unaccounted product fraction can be assigned to gaseous products, as well as volatile organic reaction products present in the aqueous phase, which are lost during the drying of the water phase residue. As the reaction temperature was increased further to 339 °C, the water residue

yield increased by 3.3 wt%, closely matching the simultaneous reduction in solid yields (41.5 wt% to 38.2 wt%), although a slight decrease in bio-crude yield (17.1 wt% to 15.9 wt%) was also experienced over the same temperature range.

The highest carbon (30.2 %) and hydrogen (27.6 %) recoveries to the biocrude were achieved at the medium reaction temperature, producing a combined bio-crude (heavy + light) with a nitrogen content of 4.0 wt%, lower than the biocrudes obtained at the other two reaction temperatures (Figure 2b). Consistent with the low overall bio-crude yield, the carbon and hydrogen recoveries obtained at 303 °C were much lower, although the difference in nitrogen recovery was much smaller, indicating that a large proportion of nitrogen-containing compounds was already incorporated into the biocrude at low reaction temperatures.

However, when increasing the reaction temperature from 322 °C to 339 °C, the hydrogen and carbon distribution to the bio-crude reduced, whereas the nitrogen retention increased, suggesting that nitrogen containing compounds continued to be converted into biocrude components at all reaction temperatures. These findings are consistent with previous studies [11, 16, 35] and suggest that significantly increasing the reaction temperatures above 320 °C had no beneficial impact on the biocrude recovery.

Contrary to trends for the biocrude, the carbon and nitrogen recoveries to the water phase reduced with increasing reaction temperatures (Figure 2c). Whilst the maximum combined carbon recovery to the water and bio-crude phases of 59.9 % was still obtained at 322 °C, the combined nitrogen recovery decreased from 77.5 % to 75.5 % as the reaction temperature was raised from 303 °C to 339 °C. A potential explanation for these trends is that the majority of nitrogen partitioned from the solid phase to the other phases at the lowest reaction temperature, whereas carbon transfer from the solid to the aqueous and bio-crude phases continued up to a temperature of 322 °C, beyond which carbon started to be lost to the gas phase. It can also be noted, that the

total nitrogen content in the aqueous phase is a very good match to the ammonium ion content, indicating that very few organic nitrogen compounds were present.

### 3.3.2 Effect of heating rate

Four different heating rates, ranging from  $10.1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $52.6\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  were obtained by varying the furnace temperature between  $500\text{ }^{\circ}\text{C}$  and  $800\text{ }^{\circ}\text{C}$ . It should be noted that these heating rates represent average, rather than absolute values, as they dropped off as the reaction temperature was approached, particularly for the lower furnace temperatures. All reactions were conducted to a maximum reaction temperature of  $320\text{ }^{\circ}\text{C}$ .

At the two lower heating rates, the solid yields remained approximately constant around 40 wt%, but increased slightly to 41.5 wt% and 42.8 wt% as the heating rates were increased to  $35.2$  and  $52.6\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , respectively (Figure 3a). Bio-crude yields, in turn, increased almost linearly from 14.9 wt% to 17.1 wt% as the heating rates were raised from  $10.1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $35.2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , but dropped off to 13.5 wt% at the highest heating rate of  $52.6\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The water residue yields showed the opposite trend to bio-crude yields, decreasing from 24.7 wt% at the lowest heating rate to 20.7 wt% at  $35.2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , before increasing to 27.7 wt% at the highest heating rate.

The increase in solid yields at the higher heating rates can be explained by the reduced reaction time, resulting in the incomplete conversion of the organic biomass components. Bio-crude and residue yields, in turn, appeared to be closely related. As heating rates increased from  $10.1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $35.2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , the product distribution shifted from water phase residue towards bio-crude, but at the highest heating rate, the bio-crude yields were at their lowest, whilst maximum water phase residue yields were obtained.

The general trend of increasing bio-crude yields with increasing heating rates is consistent with previous results by Faeth *et al.* [10], and Garcia Alba *et al.* [11]. Where the maximum bio-crude yields obtained at the highest heating rate, were significantly higher than optimized bio-crude

yields at lower sandbath temperatures [10]. A subsequent publication by the same authors [36] reported that biocrude yields increased when the total reactor loading was reduced from 60 vol% to 10 vol%. These differences were explained by an increase in the apparent biomass concentration, as the same quantity of water needed to evaporate to generate the reaction pressure. An alternative explanation is that the reactions became kinetically and heat-transfer limited as the reaction volume was increased. This could also explain the sharp drop in biocrude yields at the highest heating rate observed in the present study and suggests that the reaction time was potentially too short to achieve full conversion of the water phase residue phase into biocrude components.

As expected from the bio-crude yields, the highest carbon and hydrogen retentions were obtained at the heating rate of  $35.2\text{ }^{\circ}\text{C min}^{-1}$  (Figure 3b). The reduction in carbon, hydrogen and nitrogen retentions at lower heating rates can be attributed mostly to the reduction in bio-crude yields, whilst the overall bio-crude composition remained relatively constant. In contrast, the bio-crude obtained at the highest heating rate had a noticeably higher nitrogen content of 4.8 wt% than the bio-crude obtained at a heating rate of  $35.2\text{ }^{\circ}\text{C min}^{-1}$  (4.0 wt%). This is similar to the results obtained at the lowest reaction temperature and suggests that nitrogen containing compounds preferentially partition to the biocrude under less severe reaction conditions. It is also possible that some of this nitrogen is removed via denitrogenation reactions at higher reaction temperatures, or longer residence times, counteracting the further transfer of nitrogen containing components from the aqueous to the biocrude phase [37].

Carbon recoveries to the aqueous phase reduced from 31.9 % to 29.7 % as the heating rate was reduced from  $52.6\text{ }^{\circ}\text{C min}^{-1}$  to  $35.2\text{ }^{\circ}\text{C min}^{-1}$  (Figure 3c) and reduced further to 27.3 % for a heating rate of  $21.8\text{ }^{\circ}\text{C min}^{-1}$ . The highest combined carbon recovery to the aqueous and bio-crude phases of 59.9 % was therefore obtained at the heating rate of  $35.2\text{ }^{\circ}\text{C min}^{-1}$ , compared to recoveries of less than 55.6 % at all other heating rates. This indicates incomplete carbon transfer

from the solid to the aqueous and bio-crude phases at very high heating rates, whilst increased reaction times increased the transfer of carbon to the gas phase. In contrast, both the nitrogen recovery to the aqueous phase alone (69.4 % to 61.4 %) and combined nitrogen recovery to the aqueous and bio-crude phases (80.0 % to 71.9 %) reduced steadily as the heating rates were reduced from 52.6 °C min<sup>-1</sup> to 10.1 °C min<sup>-1</sup>. Once again, the nitrogen content in the water phase could be almost exclusively assigned to ammonium ions.

#### 3.3.2.1 *Reaction mechanism*

The trends in water phase residue and biocrude yields suggest that the two product phases are closely related. Low reaction temperatures and very high heating rates appeared to favour the formation of molecules that partition into the aqueous phase, which were further converted into biocrude as the reaction severity is increased [38]. At the same time, some of the nitrogen incorporated into the biocrude at low temperatures and high heating rates were removed via denitrogenation, reducing the nitrogen content of the bio-crude phase, and the aqueous phases, and resulting in the formation of more volatile reaction products, which were not recovered.

The results suggest a stepwise reaction mechanism; first the algae is broken up into water soluble compounds, which then further react to form the biocrude and more volatile reaction products. This is consistent with the previously suggested Maillard type reaction pathways, where carbohydrates and proteins in the biomass are first decomposed into sugars and amino acids, which then further react via dehydration reactions to form heavier, water-insoluble compounds [39, 40].

However, the algae decomposition into intermediates and their subsequent reactions to form biocrude, water phase and gaseous products, can follow many different pathways and the ultimate product distribution depends on the relative reaction kinetics between these pathways. Low heating rates would therefore favour reactions with lower activation energies, consuming a significant proportion of the reaction intermediates before the temperature rises to a level where

higher energy reactions can occur. Based on the trends observed for biocrude yields and heating rate, the reactions resulting in the formation of biocrude appear to have higher activation energies than the reactions resulting in the formation of alternative product phases.

However, at the highest heating rates, the reaction time appears to be insufficient to allow full conversion of the biomass or the reaction intermediates, resulting in a sharp drop in biocrude yields. Unfortunately, the transient batch reactors used in this study did not allow the combination of high heating rates with extended reaction times, potentially limiting the maximum biocrude yield that could be obtained. Consequently, the continuous system, which combines higher heating rates with extended reaction times, was expected to provide more favourable product distributions.

### 3.4 Continuous conversion

The continuous reaction system was operated at four different temperatures (302 °C, 320 °C, 328 °C and 344 °C) and three different flow rates (3 mL min<sup>-1</sup>, 5 mL min<sup>-1</sup> and 7 mL min<sup>-1</sup>). These conditions corresponded to heating rates ranging from 28.8 °C min<sup>-1</sup> to 67.6 °C min<sup>-1</sup>, comparable to the heating rates achieved with the batch system (10.1 °C.min<sup>-1</sup> to 52.6 °C.min<sup>-1</sup>). water

#### 3.4.1 *Effect of reaction temperature*

The effect of the reaction temperatures on the product distribution was studied at a constant system feed flow rate of 7 mL min<sup>-1</sup> (Figure 4a). Consistent with the findings from the batch study, solid yields were generally lower at higher reaction temperatures, although there was a high degree of experimental uncertainty, related to the difficulty of fully recovering the solid phase from the bottom of the reactor. Water phase residue yields followed a clearer trend, decreasing steadily from 19.8 wt% at 302 °C to 13.4 wt% at 344 °C. The trends in biocrude yields appeared to be more complex. Whilst the maximum heavy bio-crude yields (5.8 wt%) were obtained at the lowest reaction temperature of 302 °C, they decreased to a minimum of 3.5 wt% at 320 °C, before

recovering to 4.5 wt% and 5.2 wt% at reaction temperatures of 328 °C and 344 °C, respectively. Light bio-crude yields were lowest at the minimum reaction temperature of 302 °C (14.3 wt%), and remained approximately constant around 15 wt% to 16 wt% for the other three reaction temperatures.

The initial reduction in the heavy bio-crude yields from 5.8 wt% to 3.5 wt%, as the reaction temperatures were increased from 302 °C to 320 °C, closely matches the simultaneous increase in light bio-crude yields from 14.3 wt% to 16.0 wt%. This could be the result of increased cracking reactions of heavy bio-crude components to form lighter, less viscous compounds, which were carried over into the light bio-crude phase. Conversely, the subsequent increase in heavy bio-crude yields at higher reaction temperatures could be caused by the volatilisation of heavy organics bound to the solid phase product.

Based on the continuous conversion results and contrary to the batch study, the aqueous phase residue yields appeared to show little correlation to the biocrude yields. Instead the decrease in this phase could be mostly attributed to a decrease in overall recovered product from 69.5 wt% to 63.0 wt%, suggesting the formation of more volatile reaction products at higher reaction temperatures, partitioning into the gas phase, or lost during the recovery of the water phase residue. However, it is possible that these volatile products were formed from the bio-crude phase instead, as a result of gasification, denitrogenation and deoxygenation reactions, counteracting the additional conversion of the water-phase residue into the light bio-crude product phase. It should also be noted that, contrary to the batch study, bio-crude yields did not reduce at higher reaction temperatures, which could indeed suggest further conversion of the water phase residue into the light bio-crude phase.

To investigate this in more detail, the carbon, hydrogen and nitrogen balance to the bio-crude phase was calculated from the elemental analysis of the two biocrude fractions (Figure 4b). Increasing the reaction temperature from 302 °C to 320 °C resulted in a significant increase in

carbon retention from 35.0 % to 40.8 %, but at higher temperatures the carbon retention remained approximately constant. Nitrogen retentions reduced steadily from 16.3 % at 302 °C to 11.7 % at 344 °C, which is opposite to the trend observed during the batch experiments. This could suggest that the extended residence time in the continuous flow reactor allowed more denitrogenation reactions to take place. Finally, the hydrogen retention was highest at 320 °C and dropped sharply as the reaction temperature was increased further. This could be explained by the participation of hydrogen in the denitrogenation pathway to form ammonia and is consistent with the steady increase in the yield of ammonia in the water phase from 1.7 wt% to 3.0 wt%, corresponding to a nitrogen recovery of 23.2 % and 41.1 %, respectively, as the reaction temperature was raised from 302 °C to 344 °C (Supplementary information).

The carbon recovery to the water phase steadily decreased from 34.8 % to 26.8 % as the reaction temperature was increased from 302 °C to 328 °C, consisting almost exclusively of organic carbon, resulting in a combined carbon recovery to the bio-crude and water phases of 71.6 % to 64.5 %. Presumably, the remaining carbon was distributed between the solid phase, containing most of the inorganic carbon in the algae (~ 10 wt%) and the gas phase (CO<sub>2</sub>). The nitrogen recovery to the water phase ranged from 87.5% at 302 °C to 73.2 % at 328 °C, before recovering to 82.1 % at the highest reaction temperature, corresponding to combined nitrogen recoveries between 103.8 % and 86.7 %. These high mass balance closures suggest very little nitrogen distribution to the solid or gas phases.

#### *3.4.2 Effect of system flow rate*

To study the effect of the system flow rate on the product distribution, the reaction temperature was kept constant at 320 °C (Figure 5a). Increasing the flow rate from 3.0 mL min<sup>-1</sup> to 6.9 mL min<sup>-1</sup> resulted in a clear increase in solid yields from 27.7 wt% to 35.2 wt%. This is consistent with the results from the batch study, where higher heating rates were found to produce more solid, probably as a result of reduced reaction times. However, the solid yields from the continuous



system (maximum of 35.2 wt%) were much lower than those from the batch reactor (minimum of 39.7 wt%), and at the lowest flow rate approached the value of the initial algae ash content, suggesting full conversion of the organic biomass fraction. This is unsurprising, as even at the fastest flow rate, the reaction time in the continuous system (17.8 min) significantly exceeded the reaction times obtained within the batch system. Furthermore, the solid products remained in the bottom of the reactor for a period of several hours, allowing the reaction to proceed even after the algal flow was stopped. Consequently, the increase in solid yields at higher system flows cannot be solely attributed to differences in reaction times, but may instead be related to the heating rates. It should also be noted that the reaction temperature was recorded by T1 at the bottom of the inner tube, whereas the temperatures at the bottom of the reactor could have been higher, particularly for the less turbulent, lower system flow rates, which could have further impacted on the organic solids conversion.

Like the solid yields, the water phase residue yields obtained from the continuous reactor (13.8 wt% to 20.9 wt%) were significantly lower than those obtained from the batch study (20.7 wt% to 27.7 wt%) but in this instance, the residue yields increased with increasing system flow rate, whereas in the batch study they generally reduced as the heating rates were increased. Even more complex trends were obtained for the bio-crude yields. The highest amount of 'light bio-crude' was obtained at the highest flow rate of 6.9 mL min<sup>-1</sup> (17.6 wt%), dropped to a minimum of 13.9 wt% at 5.0 mL min<sup>-1</sup>, and then increased to 15.4 wt% at the lowest system flow rate. The 'heavy bio-crude' yields followed a different trend, reaching a maximum of 4.9 wt% at 3.0 mL min<sup>-1</sup>, a minimum of 3.6 wt% at 5.0 mL min<sup>-1</sup> and 4.3 wt% at 6.9 mL min<sup>-1</sup>.

A potential explanation for these trends is the contribution of both fast, competitive reactions, favoured by high heating rates, as well as slower reactions, enhanced at higher residence times, to the overall bio-crude formation. The medium flow rate of 5.0 mL min<sup>-1</sup> was too slow to realise the benefit of high heating rates, whilst the reactor residence time was too short to allow full

conversion of the components in the aqueous phase into the biocrude phase. Slower heating rates and longer reaction times may also have favoured the occurrence of polymerisation reactions, resulting in the formation of heavier bio-crude components, potentially containing greater amounts of aromatics and heteroatoms.

This is consistent with the elemental distributions to the biocrude phase obtained for the three system flow rates (Figure 5b). The bio-crude formed at 3.0 mL min<sup>-1</sup> contained a lower hydrogen and a higher nitrogen content than the bio-crude phases formed at the higher system flow rates. Even though the carbon recovery of 37.8 % was higher than at the medium flow rate, it was still lower than the carbon recovery at 6.9 mL min<sup>-1</sup> (40.8 %). Together with a much higher hydrogen, and lower nitrogen recovery, the best results, both in terms of bio-crude yields and quality, were obtained at the highest system flow rate. However, it is interesting to note that the heavy bio-crude contained a higher carbon and hydrogen and lower nitrogen content than the light bio-crude (Supplementary information).

The carbon retention to the water phase followed a similar trend to the retention in the biocrude, reaching a maximum of 30.8 % at a flowrate of 6.9 mL min<sup>-1</sup> and a minimum of 26.2 % at the medium flowrate, resulting in total carbon recoveries to the water and bio-crude phases between 58.6 % and 71.6 %. The nitrogen recovery to the water phase was also highest at the highest system flowrate (86.7 %) resulting in an overall nitrogen recovery of 101.1 %.

For the highest system flow rate, even the yields of light bio-crude on their own (17.6 wt%), exceeded the total bio-crude yields obtained from the batch reactor, which demonstrates the advantage of continuous over batch processing. Therefore, research on continuous flow reactors not only provides results which are much more applicable to large-scale industrial processing, but also has the potential to yield improved biocrude yields and product compositions.

Further analysis of the combined light bio-crude phase from all continuous reactions revealed a water content of 0.58 %, an ash content of 2.3 wt% and an energy density of 34.9 MJ kg<sup>-1</sup>.

## 4 Conclusions

Current research on the HTL of microalgae has been mostly restricted to batch reactors due to their lower cost and easier processing, compared to continuous systems. By substituting the high-pressure mechanical pumps used in previous continuous HTL studies with a nitrogen-driven feed delivery system, it was possible to design a lower-cost continuous system, allowing more industrially representative research, compared to the batch reactors commonly used on the lab scale. Data from the continuous monitoring of the system temperature profiles together with constant liquid collection volumes confirmed that the system was able to deliver a constant flow of liquid through the system, with no evidence for gas-breakthrough. In order to prevent the formation of blockages within the reactor, our design incorporated the *in-situ* collection of the solid reaction product by adapting a double-tube design, which also helped to deliver much higher heating rates, whilst providing extended reaction times. Due to the high viscosity of the biocrude at ambient conditions, it was necessary to collect the liquid product phases at elevated temperatures and pressures and control the system flow rate indirectly, using the outflow of nitrogen and reaction gases from the product collection pots. Using this system it was possible to consistently process 1 L of a 5 wt% wastewater-derived algae slurry.

Results from the batch study confirmed previous work in the literature, which suggested that increased heating rates could help to improve biocrude yields. This was attributed to the conversion of unstable aqueous phase intermediates during the heating process to form undesired solid or gaseous by-products, before sufficient reaction temperatures were reached to start the bio-crude formation process. Nevertheless, at very high heating rates, biocrude yields reduced sharply and this was ascribed to very short reaction times, insufficient to achieve full biomass conversion.

These limitations were not present within the continuous reaction system, which combined fast heating rates with extended reaction times. Consequently, this system was able to produce much

higher biocrude yields and lower solid and water phase residue yields than the batch system. Consistent with previous literature findings, the best results were obtained at the highest system flow rate, although the results suggested a competitive effect on bio-crude formation between fast reactions, favoured by high heating rates, and slower reactions, enhanced at higher reactor residence times.

Although maximum overall bio-crude yields of 21.9 wt% in this study were relatively low, this can be ascribed to a very high algal ash content of 29.9 wt%, together with a low lipid fraction of 7.9 wt%. Given the low cost of this feedstock, the combination of algal wastewater treatment with fuel production via HTL represents a promising economic process, which warrants further investigation.

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## References

1. S. Raikova, C. D. Le, J. L. Wagner, V. P. Ting and C. J. Chuck, in *Biofuels for Aviation - Feedstocks, Technology and Implementation*, ed. C. J. Chuck, Elsevier, London, 2016.
2. Elliott, D.C., Review of recent reports on process technology for thermochemical conversion of whole algae to liquid fuels. *Algal Res.*, 2016. 13: p. 255-263.

3. D. López Barreiro, W. Prins, F. Ronsse and W. Brilman, Hydrothermal liquefaction (HTL) of microalgae for biofuel production: state of the art review and future prospects. *Biomass Bioenerg.* 2013, 53, 113-127.
4. L. Xu, D. W. Wim Brilman, J. A. Withag, G. Brem and S. Kersten, Assessment of a dry and a wet route for the production of biofuels from microalgae: energy balance analysis. *Bioresource Technol.*, 2011, 102, 5113-5122.
5. P. Biller, A. B. Ross, S. C. Skill, A. Lea-Langton, B. Balasundaram, C. Hall, R. Riley and C. A. Llewellyn. Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. *Algal Res.*, 2012, 1, 70-76.
6. U. Jena, N. Vaidyanathan, S. Chinnasamy and K. C. Das, Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass. *Bioresource Technol.*, 2011, 102, 3380-3387.
7. L. Garcia Alba, C. Torri, D. Fabbri, S. R. A. Kersten and D. W. F. Brilman, Microalgae growth on the aqueous phase from hydrothermal liquefaction of the same microalgae *Chem. Eng. J.* 2013, 228, 214-223.
8. C. J. Chuck, J. L. Wagner and R. W. Jenkins, in *Chemical Processes for a Sustainable Future*, eds. T. M. Letcher, J. L. Scott and D. A. Patterson, Royal Society of Chemistry, Cambridge, 2015, ch. 16, pp. 425-442.
9. Elliott, D.C., et al., Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresource Technol.*, 2015. 178: p. 147-56.
10. J. L. Faeth, P. J. Valdez and P. E. Savage. Fast hydrothermal liquefaction of *Nannochloropsis* sp. to produce biocrude. *Energ. Fuel.* 2013, 27, 1391-1398.
11. L. Garcia Alba, C. Torri, C. Samori, J. van der Spek, D. Fabbri, S. R. A. Kersten and D. W. F. Brilman. Hydrothermal treatment (HTT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept. *Energ. Fuel.*, 2012, 26, 642-657.
12. A. Cole, Y. Dinburg, B. S. Haynes, Y. He, M. Herskowitz, C. Jazrawi, M. Landau, X. Liang, M. Magnusson, T. Maschmeyer, A. F. Masters, N. Meiri, N. Neveux, R. de Nys, N. Paul, M. Rabaev, R. Vidruk-Nehemya and A. K. L. Yuen. From macroalgae to liquid fuel via waste-water remediation, hydrothermal upgrading, carbon dioxide hydrogenation and hydrotreating. *Energy Environ. Sci.*, 2016, 9, 1828-1840.
13. J. L. Garcia-MoscOSO, W. Obeid, S. Kumar and P. G. Hatcher, Flash hydrolysis of microalgae (*Scenedesmus* sp.) for protein extraction and production of biofuels intermediates. *J. Supercrit. Fluid.*, 2013, 82, 183-190.

14. P. Biller, B. K. Sharma, B. Kunwar and A. B. Ross. Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae. *Fuel*, 2015, 159, 197-205.
15. B. Patel and K. Hellgardt. Hydrothermal upgrading of algae paste in a continuous flow reactor. *Bioresource Technol.*, 2015, 191, 460-468.
16. C. Jazrawi, P. Biller, A. B. Ross, A. Montoya, T. Maschmeyer and B. S. Haynes. Pilot plant testing of continuous hydrothermal liquefaction of microalgae. *Algal Res.*, 2013, 2, 268-277.
17. D. C. Elliott, T. R. Hart, A. J. Schmidt, G. G. Neuenschwander, L. J. Rotness, M. V. Olarte, A. H. Zacher, K. O. Albrecht, R. T. Hallen and J. E. Holladay. Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. *Algal Res.*, 2013, 2, 445-454.
18. D. L. Barreiro, B. R. Gómez, U. Hornung, A. Kruse and W. Prins. Hydrothermal liquefaction of microalgae in a continuous stirred-tank reactor. *Energ. Fuel.*, 2015, 29, 6422-6432.
19. C. M. Beal, L. N. Gerber, D. L. Sills, M. E. Huntley, S. C. Machesky, M. J. Walsh, J. W. Tester, I. Archibald, J. Granados and C. H. Greene. Algal biofuel production for fuels and feed in a 100-ha facility: A comprehensive techno-economic analysis and life cycle assessment. *Algal Res.*, 2015, 10, 266-279.
20. N. D. Orfield, Doctor of Philosophy PhD Thesis, University of Michigan, 2013.
21. R. Sayre. Microalgae: the potential for carbon capture. *BioScience*, 2010, 60, 722-727.
22. M. K. Lam and K. T. Lee. Microalgae biofuels: a critical review of issues, problems and the way forward. *Biotechnol. Adv.*, 2012, 30, 673-690.
23. M. K. Lam, K. T. Lee and A. R. Mohamed. Current status and challenges on microalgae-based carbon capture. *Int. J. Greenhouse Gas Control*, 2012, 10, 456-469.
24. S. Raikova, H. Smith-Baedorf, R. Bransgrove, O. Barlow, F. Santomauro, J. L. Wagner, M. J. Allen, C. G. Bryan, D. Sapsford and C. J. Chuck. Assessing hydrothermal liquefaction for the production of bio-oil and enhanced metal recovery from microalgae cultivated on acid mine drainage. *Fuel Process. Technol.*, 2016, 142, 219-227.
25. R. J. Craggs, S. Heubeck, T. J. Lundquist and J. R. Benemann. Algal biofuels from wastewater treatment high rate algal ponds. *Water Sci Technol.*, 2011, 63, 660-665.
26. A. Kumar, S. Ergas, X. Yuan, A. Sahu, Q. Zhang, J. Dewulf, F. X. Malcata and H. van Langenhove. Enhanced CO<sub>2</sub> fixation and biofuel production via microalgae: recent developments and future directions. *Trends Biotechnol.*, 2010, 28, 371-380.

- 717 27. Aquastat, Food and Agriculture Organization of the United Nations, 2014. Available  
718 from: <http://www.fao.org/nr/water/aquastat/wastewater/index.stm> [28/08/2014].
- 719 28. Cogan, M. and B. Antizar-Ladislao, The ability of macroalgae to stabilise and optimise  
720 the anaerobic digestion of household food waste. *Biomass Bioenerg.*, 2016. 86: p. 146-  
721 155.
- 722 29. K. A. C. C. Taylor. A modification of the phenol/sulfuric acid assay for total  
723 carbohydrates giving more comparable absorbances *Appl. Biochem. Biotech.*, 1995, 53,  
724 207-214.
- 725 30. E. T. Kostas, D. A. White, C. Du and D. J. Cook, Selection of yeast strains for bioethanol  
726 production from UK seaweeds. *J. Appl. Phycol.*, 2016, 28, 1427-1441.
- 727 31. J. Wagner, R. Bransgrove, T. A. Beacham, M. J. Allen, K. Meixner, B. Drosig, V. P. Ting  
728 and C. J. Chuck. Co-production of bio-oil and propylene through the hydrothermal  
729 liquefaction of polyhydroxybutyrate producing cyanobacteria. *Bioresource Technol.*,  
730 2016, 207, 166-174.
- 731 32. F. Mariotti, D. Tome and P. P. Mirand. Converting nitrogen into protein—beyond 6.25  
732 and Jones' factors *Crit. Rev. Food Science Nutrition*, 2008, 48, 177-184.
- 733 33. A.B. Ross, J.M. Jones, M.L. Kubacki, T. Bridgeman, Classification of macroalgae as fuel  
734 and its thermochemical behaviour. *Bioresource Technol.*, 2008. 99(14): p. 6494-504.
- 735 34. X. Cheng, M. D. Ooms and D. Sinton, Biomass-to-biocrude on a chip via hydrothermal  
736 liquefaction of algae. *Lab on a Chip*, 2016, 16, 256-260.
- 737 35. C. Torri, L. Garcia Alba, C. Samori, D. Fabbri and D. W. F. Brilman. Hydrothermal  
738 treatment (HTT) of microalgae: detailed molecular characterization of HTT oil in view of  
739 HTT mechanism elucidation. *Energ. Fuel.*, 2012, 26, 658-671.
- 740 36. J. L. Faeth, P. E. Savage, J. M. Jarvis, A. M. McKenna and P. E. Savage.  
741 Characterization of products from fast and isothermal hydrothermal liquefaction of  
742 microalgae. *AIChE J.* 2016, 62, 815-828.
- 743 37. C. Tian, Z. Liu, Y. Zhang, B. Li, W. Cao, H. Lu, N. Duan. Hydrothermal liquefaction of  
744 harvested high-ash low-lipid algal biomass from Dianchi Lake: effects of operational  
745 parameters and relations of products. *Bioresource Technol.*, 2015. 184: p. 336-43.
- 746 38. W.T. Chen, Y. Zhang, J. Zhang, G. Yu, L.C. Schideman. Hydrothermal liquefaction of  
747 mixed-culture algal biomass from wastewater treatment system into bio-crude oil.  
748 *Bioresource Technol.*, 2014. 152: p. 130-9.
- 749 39. S. S. Toor, L. Rosendahl and A. Rudolf, Hydrothermal liquefaction of biomass: a review  
750 of subcritical water technologies. *Energy*, 2011, 36, 2328-2342.

751 40. W. Yang, X. Li, Z. Li, C. Tong and L. Feng. Understanding low-lipid algae hydrothermal  
752 liquefaction characteristics and pathways through hydrothermal liquefaction of algal  
753 major components: Crude polysaccharides, crude proteins and their binary  
754 mixtures. *Bioresource Technol.*, 2015, 196, 99-108.  
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## Figure legends

Table 1: Proximate and ultimate analysis of wastewater algae

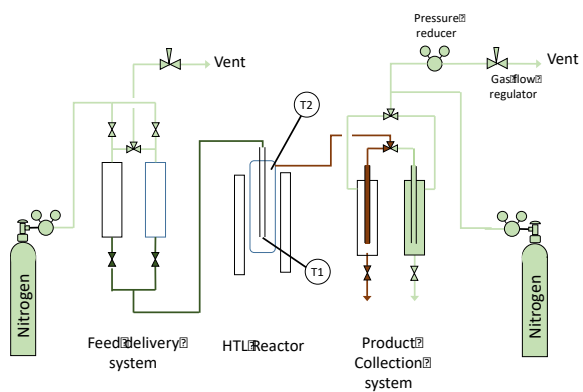
Figure 1: Process schematic for continuous HTL system

Figure 2: Effect of reaction temperature on the batch conversion of wastewater-derived algae; (a) overall product distribution, (b) CHN retention in biocrude, (c) CN retention in aqueous phase, calculated from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent the standard deviations of three repeats

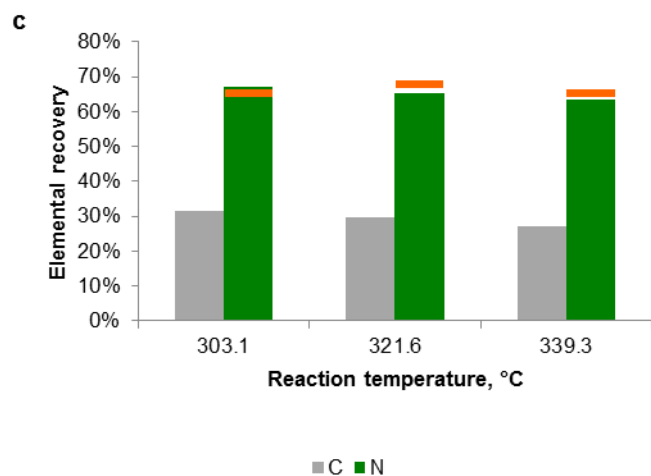
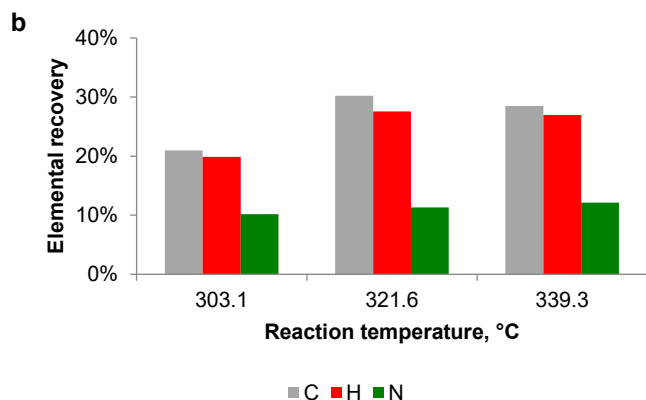
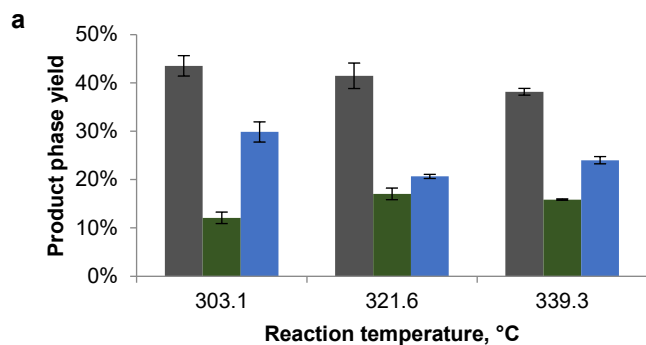
Figure 3: Effect of heating rate on the batch conversion of wastewater-derived algae; (a) overall product distribution, (b) CHN retention in biocrude, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent the standard deviations of three repeats.

Figure 4: Effect of reaction temperature on the continuous liquefaction of wastewater algae; (a) overall product distribution, (b) CHN retention in bio-crude, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent standard deviation of two repeats conducted at 320 °C.

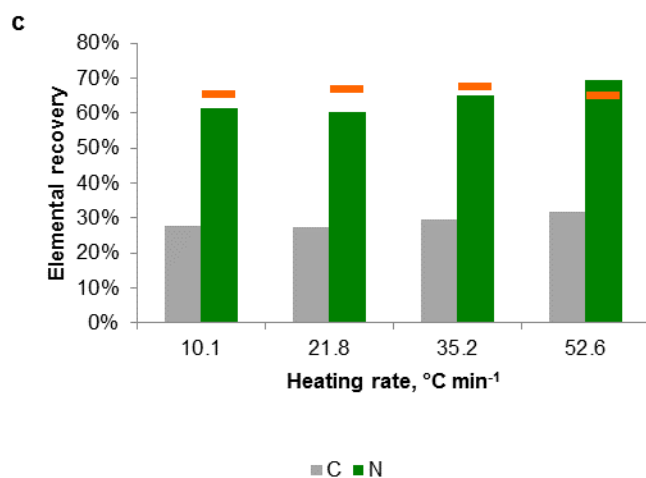
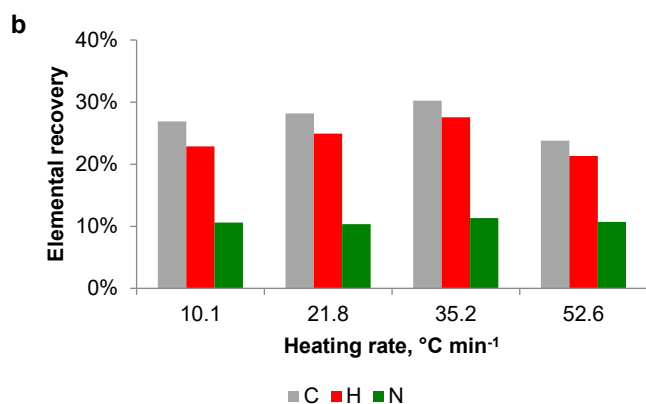
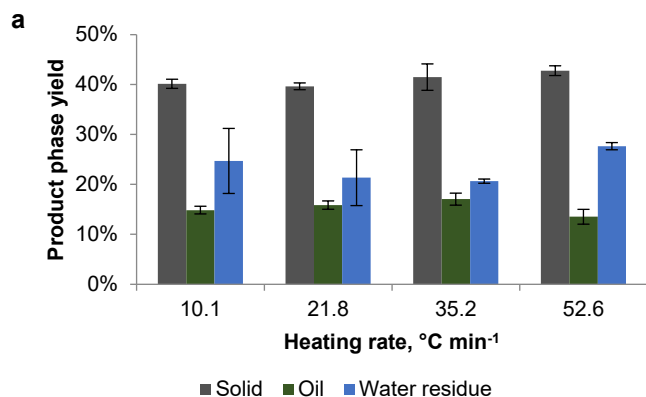
Figure 5: Effect of feed flowrate on the continuous liquefaction of wastewater algae; (a) overall product distribution, (b) CHN retention in bio-crude, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent standard deviation of two repeats conducted at highest flowrate.



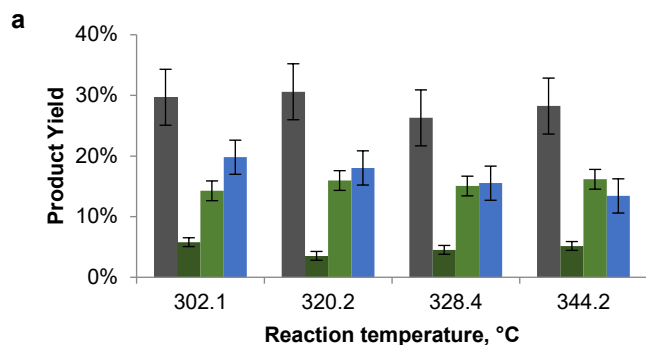
**Figure 1: Process schematic for continuous HTL system**



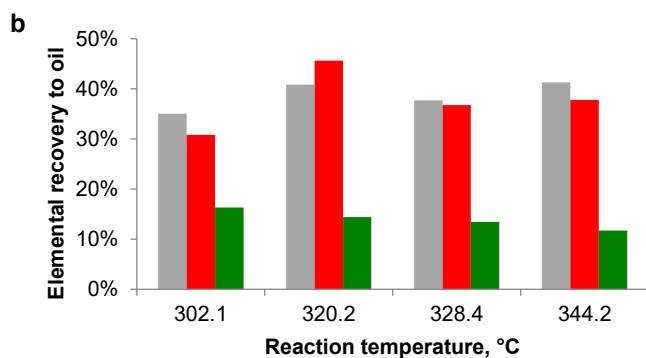
**Figure 2: Effect of reaction temperature on the batch conversion of wastewater-derived algae; (a) overall product distribution, (b) CHN retention in biocrude, (c) CN retention in aqueous phase, calculated from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent the standard deviations of three repeats.**



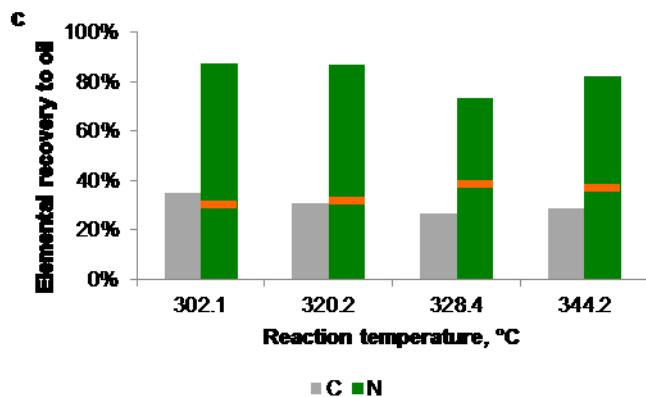
**Figure 3: Effect of heating rate on the batch conversion of wastewater-derived algae; (a) overall product distribution, (b) CHN retention in biocrude, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent the standard deviations of three repeats.**



■ Solid ■ Heavy Oil ■ Light Oil ■ Water phase residue



■ Carbon ■ Hydrogen ■ Nitrogen



■ C ■ N

Figure 4: Effect of reaction temperature on the continuous liquefaction of wastewater algae; (a) overall product distribution, (b) CHN retention in bio-oil, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent standard deviation of two repeats conducted at 320 °C.

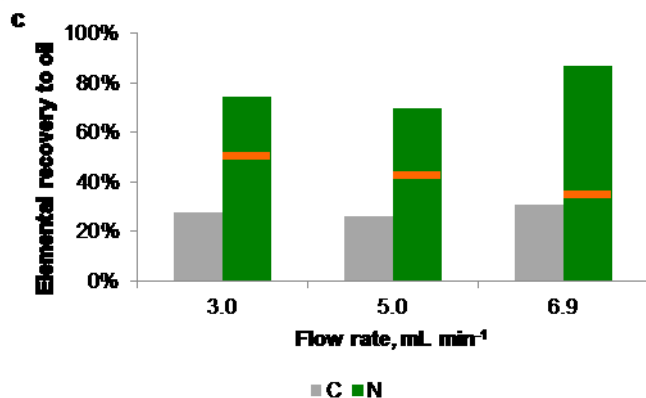
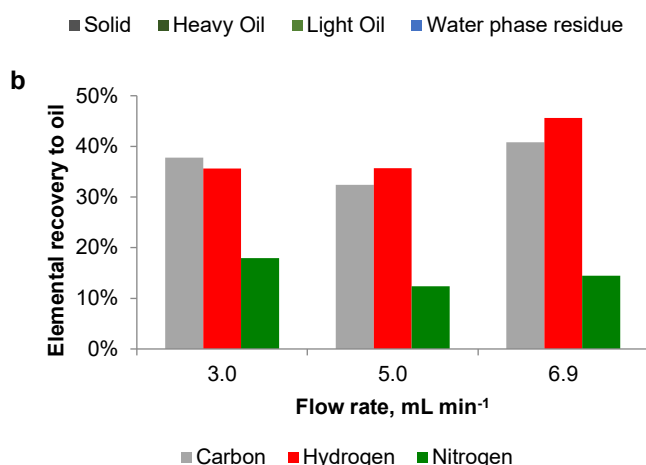
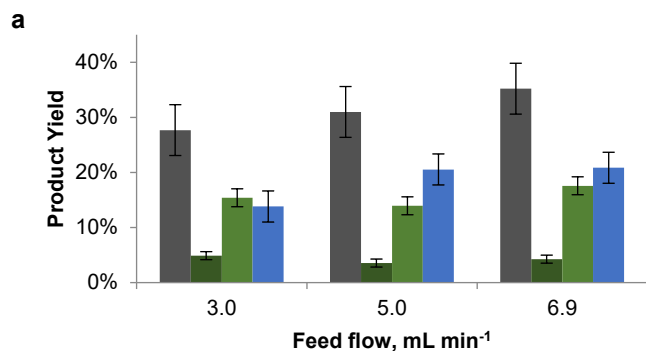


Figure 5: Effect of feed flowrate on the continuous liquefaction of wastewater algae; (a) overall product distribution, (b) CHN retention in bio-oil, (c) CN retention to aqueous-phase from TOC and TN analysis, with the results from ammonium ion analysis superimposed as orange markers. Error bars represent standard deviation of two repeats conducted at highest flowrate.

